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DIELECTRIC LOSS AND RELAXATION – II

The description of dielectric loss and relaxation with emphasis on materials in the condensed phase is continued in this chapter. We begin with Jonscher's universal law which is claimed to apply to all dielectric materials. Distinction is made here between dielectrics that show negligible conduction currents and those through which appreciable current flows by carrier transport. Formulas for relaxation are given by Jonscher for each case. Again, this is an empirical approach with no fundamental theory to backup the observed frequency dependence of ϵ'' according to a power law. The relatively recent theory of Hill and Dissado, which attempts to overcome this restriction, is described in considerable detail. A dielectric may be visualized as a network of passive elements as far as the external circuit is concerned and the relaxation phenomenon analyzed by using the approach of equivalent circuits is explained. This method, also, does not provide further insight into the physical processes within the dielectric, though by a suitable choice of circuit parameters we can reasonably reproduce the shape of the loss curve. Finally, an analysis of absorption in the optical frequency range is presented both with and without electron damping effects.

4.1 JONSCHER'S UNIVERSAL LAW

On the basis of experimentally observed similarity of the ω - ϵ'' curves for a large number of polymers, Jonscher¹ has proposed an empirical "Universal Law" which is supposed to apply to all dielectrics in the condensed phase. Let us denote the exponents at low frequency and high frequency as m and n respectively. Here low and high frequency have a different connotation than that used in the previous chapter. Both low and high frequency refer to the post-peak frequency. The loss factor in terms of the susceptibility function is expressed as

$$\frac{1}{\chi''} = \left(\frac{\omega}{\omega_2}\right)^{-m} + \left(\frac{\omega}{\omega_1}\right)^{1-n} \quad (4.1)$$

where $1/\omega_1$ and $1/\omega_2$ are well defined, thermally activated frequency parameters. The empirical exponents m and n are both less than one and m is always greater than $1-n$ by a factor between 2 and 6 depending on the polymer and the temperature, resulting in a pronounced asymmetry in the loss curve. Both m and n decrease with decreasing temperature making the loss curve broader at low temperatures when compared with the loss curve at higher temperatures. In support of his equation Jonscher points out that the low temperature β -relaxation peak in many polymers is much broader and less symmetrical than the high temperature α -relaxation peak.

In addition to polymers the dielectric loss in inorganic materials is associated with hopping of charge carriers, to some extent, and the loss in a wide range of materials is thought to follow relaxation laws of the type:

For $\omega \gg \omega_p$

$$\chi'' = \cot\left(\frac{n\pi}{2}\right) \chi' \propto \omega^{n-1} \quad (4.2)$$

For $\omega \ll \omega_p$

$$\chi'' = \tan\left(\frac{m\pi}{2}\right) [\chi_s - \chi'] \propto \omega^m \quad (4.3)$$

where the exponents fall within the range

$$0 < m < 1$$

$$0 < n < 1$$

The physical picture associated with hopping charges between two localized sites is explained with the aid of fig. 3-5 of the previous chapter. This picture is an improvement over the bistable model of Debye. A positive charge $+q$ occupying site i can jump to the adjacent site j which is situated at a distance r_{ij} . The frequency of jumps between the two sites is the Debye relaxation frequency $1/\tau_D$ and the loss resulting from this mechanism is given by Debye equation for ϵ'' . τ_D is a thermally activated parameter.

In Jonscher's model some of the localised charge may jump over several consecutive sites leading to a d.c. conduction current and some over a shorter distance; hopping to the adjacent site becomes a limiting case. A charge in a site i is a source of potential. This potential repels charges having the same polarity as the charge in site i and attracts those of opposite polarity. The repulsive force screens partially the charge in question and the result of screening is an effective reduction of the charge under consideration.

In a gas the charges are free and therefore the screening is complete, with the density of charge being zero outside a certain radius which may be of the order of few Debye lengths. In a solid, however, the screening would not be quite as complete as in a gas because the localised charges are not completely free to move. However, Jonscher proposed that the screening would reduce the effective charge to pq where p is necessarily less than one.

Let us now assume that the charge jumps to site j at $t=0$. The screening charge is still at site i and the initial change of polarization is qr_{ij} . The screening readjusts itself over a time period τ , the time required for this adjustment is visualized as a relaxation time, τ . As long as the charge remains in its new position longer than the relaxation time as defined in the above scheme, ($\tau < \tau_D$), there is an energy loss in the system².

The situation $\tau > \tau_d$ is likely to occur more often, and presents a qualitatively different picture, though the end result will not be much different. The screening effect can not follow instantly the hopping charge but attains a time averaged occupancy between the two sites. The electric field influences the occupancy rate; down-field rate is enhanced and up-field occupancy rate is decreased. The setting up of the final value of polarization is associated with an energy loss.

According to Jonscher two conditions should be satisfied for a dielectric to obey the universal law of relaxation:

1. The hopping of charges must occur over a distance of several sites, and not over just adjacent sites.
2. The presence of screening charge must adjust slowly to the rapid hopping.

In the model proposed by Jonscher screening of charges does not occur in ideal polar substances because there is no net charge transfer. In real solids, however, both crystalline and amorphous, the molecules are not completely free to change their orientations but they must assume a direction dictated by the presence of dipoles in the vicinity. Because the dipoles have finite length in real dielectrics they are more rigidly fixed, as in the case of a side group attached to the main chain of a polymer. The dipoles act as though they are pinned at one end rather than completely free to change

orientation by pure orientation. The swing of the dipole about its fixed end is equivalent to the hopping of charge and satisfies condition 1 set above, though less effectively.

The essential feature of the universal law is that the post-peak variation of χ'' is according to eq. (4.2) or superpositions of two such functions with the higher frequency component having a value of n closer to unity. The exponents m and n are weakly dependent on temperature, decreasing with increasing temperature. Many polymeric materials, both polar and non-polar, show very flat losses over many decades of frequency, with superposed very weak peaks. This behavior is consistent with $n \approx 1$, not at all compatible with Debye theory of ω^{-1} dependence. From eq. (4.2) we note that,

$$\frac{\chi''}{\chi'} = \cot\left(\frac{n\pi}{2}\right) \quad (4.4)$$

As a consequence of equation (4.2) the ratio χ''/χ' in the high frequency part of the loss peak remains independent of the frequency. This ratio is quite different from Debye relaxation which gives $\chi''/\chi' = \omega\tau$. Therefore in a log-log presentation $\chi' - \omega$ and $\chi'' - \omega$ are parallel.

For the low frequency range of the loss peak, equation (4.3) shows that

$$\frac{\chi''}{\chi_s - \chi'} = \tan\frac{m\pi}{2} \quad (4.5)$$

The denominator on the left side of equation (4.5) is known as the dielectric decrement, a quantity that signifies the decrease of the dielectric constant as a result of the applied frequency. Combining equations (4.2) and (4.3) the susceptibility function given by equation (4.1) is obtained. The range of frequency between low frequency and high frequency regions is narrow and the fit in that range does not significantly influence the representation significantly over the entire frequency range. In any case, as pointed out earlier, these representations lack any physical reality and the approach of Dissado-Hill^{3,4} assumes greater significance for their many-body theory which resulted in a relaxation function that has such significance.

Jonscher identifies another form of dielectric relaxation in materials that have considerable conductivity. This kind of behavior is called quasi-dc process (QDC). The frequency dependence of the loss factor does not show a peak and raises steadily towards lower frequencies. For frequencies lower than a critical frequency, $\omega \leq \omega_c$ the complex part of the susceptibility function, χ'' , obeys a power law of type ω^{p-1} . Here the

real part, χ' , also obeys a power law for frequencies $\omega \leq \omega_c$, as shown in fig. 4.1. Here ω_c represents threshold frequency not to be confused with ω_p . In the low frequency region $\chi'' > \chi'$ and in this range of frequencies the material is highly lossy. The curves of χ' and χ'' intersect at ω_c . The characteristics for QDC are represented as:

$$\chi' \propto \chi'' \propto \omega^{m-1} \quad \text{for } \omega \ll \omega_c \quad (4.6)$$

$$\chi' \propto \chi'' \propto \omega^{n-1} \quad \text{for } \omega \gg \omega_c \quad (4.7)$$

To overcome the objection that the universal relaxation law, like Cole-Cole and Davidson-Cole, is empirical, Jonscher proposed an energy criterion as a consequence of equation (4.4)

$$\frac{W_L}{W_s} = \cot\left(\frac{n\pi}{2}\right) \quad (4.8)$$

in which W_L is the energy lost per radian and W_s is the energy stored. In a field of magnitude E_{rms} the energy lost per radian per unit volume is $\epsilon_0 \chi'' E_{rms}^2$ and the power lost is σE_{rms}^2 . The alternating current (a.c.) conductivity is

$$\sigma_{ac} = \sigma_{dc} + \epsilon_0 \omega \chi'' \quad (4.9)$$

where σ_{dc} is the d.c. conductivity. This equation defines the relationship between the ac conductivity in terms of χ'' . We shall revert to a detailed discussion of conductivity shortly.

The energy criterion of Jonscher is based on two assumptions. The first one is that the dipolar orientation or the charge carrier transition occurs necessarily by discrete movements. Second, every dipolar orientation that contributes to χ' makes a proportionate contribution to χ'' . Note that the right sides of equations (4.4) and (4.5) are independent of frequency to provide a basis for the second assumption. Several processes such as the losses in polymers, dipolar relaxation, charge trapping and QDC have been proposed to support the energy criterion. Fig. (4.1c) shows the nearly flat loss in low loss materials. Fig. 4.1(d) applies to H-N equation.

Though we have considered materials that show a peak in $\epsilon'' - \log \omega$ curve the situation shown in fig. 4.1(c) demands some clarification. The presence of a peak implies that at frequencies ($\omega < \omega_p$) the loss becomes smaller and smaller till, at $\omega = 0$, we obtain $\epsilon'' =$

0, which of course is consistent with the definition of the loss factor (fig. 3.1). There are a number of materials which altogether show a different kind of response; in these materials the loss factor, instead of decreasing with decreasing frequency, shows a trend increasing with lower frequencies due to the presence of dc conductivity which makes a contribution to ϵ'' according to equation (4.9). The conductivity here is attributed to partially mobile, localised charge carriers.

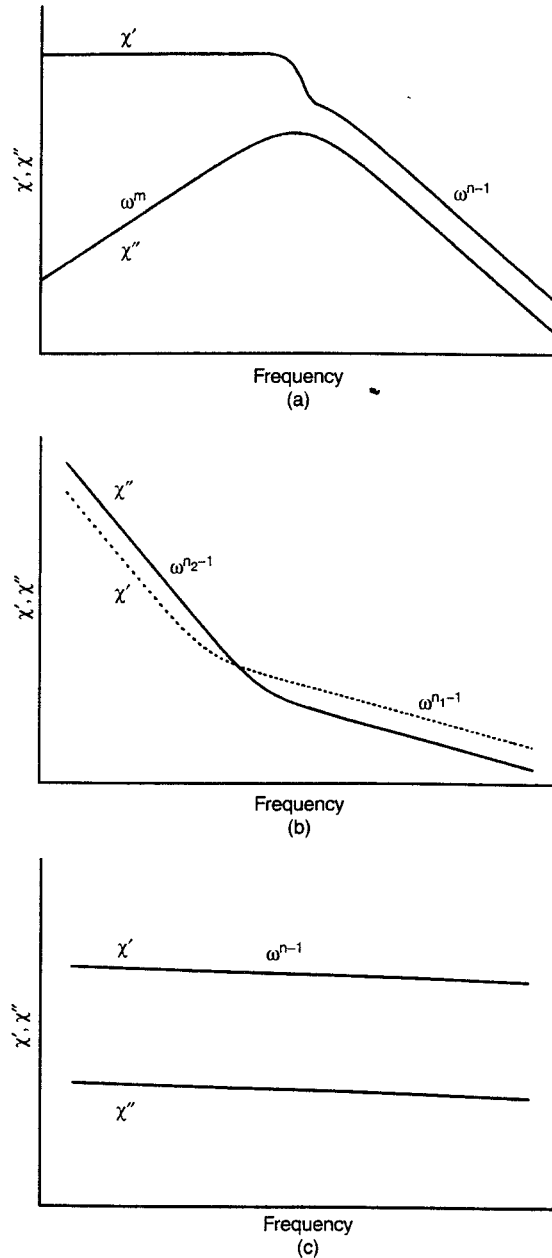


Fig. 4.1 Frequency dependencies of “universal” dielectric response for: (a) dipolar system, (b) quasi-dc (QDC) or low frequency dispersion (LFD) process, and (c) flat loss in low-loss material (Das-Gupta and Scarpa⁵ © 1999, IEEE).

As opposed to the small contribution of the free charge carriers to the dielectric loss, localized charge carriers make a contribution to the dielectric loss at low frequencies that must be taken into account. Jonscher⁶ discusses two different mechanisms by which localized charges contribute to dielectric relaxation. In the first mechanism, application of a voltage results in a delayed current response which is interpreted in terms of the delayed release of localized charges to the appropriate band where they take part in the conduction process. If the localized charge is an electron it is released to the conduction band. If the localized charge is a hole, then it is released to a valence band.

The second mechanism is that the localized charge may just be transferred by the applied field to another site not involving the conduction band or valence band. This hopping may be according to the two potential well models described earlier in section 3.4. The hopping from site to site may extend throughout the bulk, the sites forming an interconnected net work which the charges may follow. Some jumps are easier because of the small distance between sites. The easier jumps contribute to dielectric relaxation whereas the more difficult jumps contribute to conduction, in the limit the charge transfer to the free band being the most challenging.

This picture of hopping charges contributing both to dielectric relaxation and conduction is considered feasible because of the semi-crystalline and amorphous nature of practical dielectrics. With increasing disorder the density of traps increases and a completely disordered structure may have an unlimited number of localized levels. The essential point is that the dielectric relaxation is not totally isolated from the conductivity.

Dielectric systems that have charge carriers show an ac conductivity that is dependent on frequency. A compilation of conductivity data by Jonscher over 16 decades leads to the conclusion that the conductivity follows the power law

$$\sigma_{ac} = \sigma_{dc} + A\omega^n \quad (4.10)$$

where A is a constant and the exponent n has a range of values between 0.6 and 1 depending on the material. However there are exceptions with n having a value much lower than 0.6 or higher than one.

A further empirical equation due to Hill-Jonscher which has not found wide applicability is⁷:

$$\varepsilon^* = \varepsilon_{\infty} + (\varepsilon_s - \varepsilon_{\infty}) {}_2F^1(m, n, \omega\tau) \quad (4.11)$$

where

$$F(m, n, \omega\tau) = (1 + j\omega\tau)^{n-1} {}_2F^1\left(1-n, 1-m; \frac{1}{1+j\omega\tau}\right) \quad (4.12)$$

and ${}_2F^1$ is the Gaussian hypergeometric function.

4.2 CLUSTER APPROACH OF DISSADO-HILL

Dissado-Hill (1983) view matter in the condensed phase as having some structural order and consequently having some locally coupled vibrations. Dielectric relaxation is the reorganizations of the relative orientations and positions of constitutive molecules, atoms or ions. Relaxation is therefore possible only in materials that possess some form of structural disorder.

Under these circumstances relaxation of one entity can not occur without affecting the motion of other entities, though the entire subject of dielectric relaxation was originated by Debye who assumed that each molecule relaxed independent of other molecules. This clarification is not to be taken as criticism or over-stressing the limitation of Debye theory. In view of the inter-relationship of relaxing entities the earlier approach should be viewed as an equivalent instantaneous description of what is essentially a complex dynamic phenomenon. The failure to take into account the local vibrations has been attributed to the incorrect description of the dielectric response in the time domain, as will be discussed later⁸.

The theory of Dissado-Hill⁹ has basis on a realistic picture of the nature of the structure of a solid that has imperfect order. They pictured that the condensed phase, both solids and liquids, which exhibit position or orientation relaxation, are composed of spatially limited regions over which a partially regular structural order of individual units extends. These regions are called clusters. In any sample of the material many clusters exist and as long as interaction between them exists an array will be formed possessing at least a partial long range regularity. The nature of the long range regularity is bounded by two extremes. A perfectly regular array as in the case of a crystal, and a gas in which there is no coupling, leading to a cluster gas. The clusters may collide without assimilating and dissociating. These are the extremes. Any other structure in between in the condensed phase can be treated without loss of generality with regard to microscopic structure and macroscopic average.

In the model proposed by them, orientation or position changes of individual units such as dipole molecules can be accomplished by the application of electric field. The electric

field is usually spatially uniform over the material under study and will influence the orientation or position fluctuations, or both, that are also spatially in phase. When the response is linear, the electric field will only change the population of these fluctuations and not their nature.

The displacement fluctuations may be of two kinds, inter-cluster or intra-cluster. Each of these interactions makes its own characteristic contribution to the susceptibility function. The intra-cluster (within a cluster) movement involves individual dipoles which relaxes according to an exponential law ($e^{-t/\tau}$), which is the Debye model. The dipole is linked to other dipoles through the structure of the material and therefore the relaxing dipole will affect the field seen by other dipoles of the cluster. The neighboring dipoles may also relax exponentially affecting the field seen by the first dipole. The overall effect will be an exponential single dipole relaxation.

On the other hand, the inter-cluster (between adjacent clusters) movement will occur through dipoles at the edges of neighboring clusters (Fig. 4.2¹⁰). The inter-cluster motion has a larger range than the intra-cluster motion. The structural change that occurs because of these two types of cluster movements results in a frequency dependent response of the dielectric properties. Proceeding from these considerations Dissado and Hill formulate an improved rate equation and determine its solution by quantum mechanical methods.

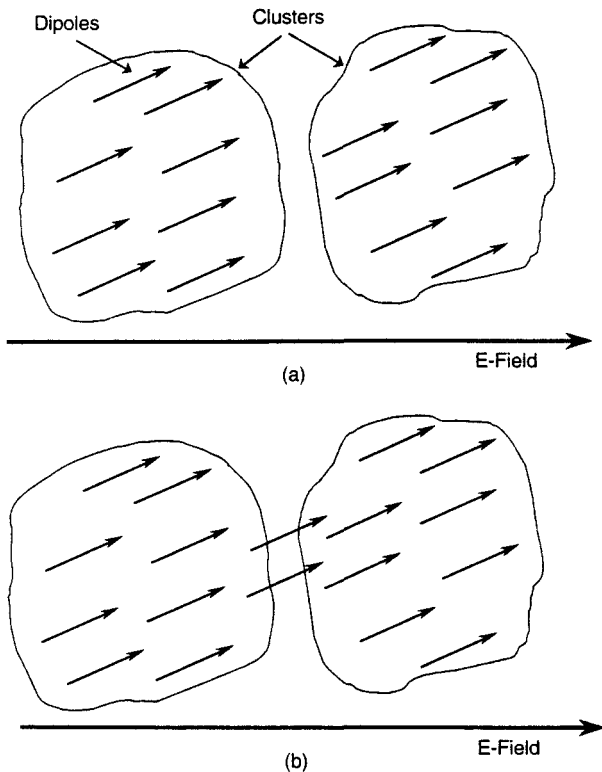


Fig. 4.2 Schematic diagram of (a) intra-cluster motion and (b) inter-cluster exchange mechanism in the Dissado-Hill cluster model for dielectric relaxation (Das Gupta and Scarpa, 1999) (with permission of IEEE).

The theory of Dissado and Hill is significant in that the application of their theory provides information on the structure of the material, though on a coarse scale. The inter-cluster displacement arises from non-polar structural fluctuations whereas the intra-cluster motion is necessarily dipolar. Highly ordered structures in which the correlation of clusters is complete can be distinguished from materials with complete disorder.

The range of materials for which relaxations have been observed is extensive, running from covalent, ionic or Van der Waal crystals at one extreme, through glassy or polymer matrices to pure liquids and liquid suspensions at the other. The continued existence of cluster structure in the viscous liquid formed from the glass, to above a glass transition¹¹ has been demonstrated. Applications to plastic crystal phases¹² and ferroelectrics have also been made. The theory of Dissado-Hill should be considered a major step forward in the development of dielectric theory and has the potential of yielding rich information when applied to polymers.

4.3 EQUIVALENT CIRCUITS

A real dielectric may be represented by a capacitance in series with a resistance, or alternatively a capacitance in parallel with a resistance. We consider that this representation is successful if the frequency response of the equivalent circuit is identical to that of the real dielectric. We shall soon see that a simple equivalency such as a series or parallel combination of resistance and capacitance may not hold true over the entire frequency and temperature domain.

4.3.1 A SERIES EQUIVALENT CIRCUIT

A capacitance C_s in series with a resistance has a series impedance given by

$$Z_s = R_s + \frac{1}{j\omega C_s} \quad (4.13)$$

The impedance of the capacitor with the real dielectric is

$$Z = \frac{1}{j\omega C_0(\epsilon' - j\epsilon'')} \quad (4.14)$$

where C_0 is the capacitance without the dielectric. Since the two impedances are equal from the external circuit point of view we can equate equations (4.13) and (4.14). To obtain ϵ' and ϵ'' as a function of frequency we equate the real and imaginary parts. This gives

$$\epsilon' = \frac{C_s}{C_0[1 + (\omega R_s C_s)^2]} \quad (4.15)$$

$$\epsilon'' = \frac{\omega R_s C_s^2}{C_0[1 + (\omega R_s C_s)^2]} \quad (4.16)$$

$$\tan \delta = \omega R_s C_s \quad (4.17)$$

According to equation (4.16) the ϵ'' - ω characteristics show a broad maximum at the radian frequency corresponding to $\omega C_s R_s = 1$. Substituting $C_s R_s = \tau$ the condition for maximum ϵ'' translates into $\omega \tau = 1$. τ is the relaxation time which substitutes for the time constant in electrical engineering applications.

Qualitative agreement of the shape of ϵ'' - ω curve with the measured dielectric loss does not justify the conclusion that the series equivalent circuit can be used to represent all polar dielectrics. We therefore consider other equivalent circuits to obtain a comprehensive picture of the scope and limitations of the equivalent circuit approach.

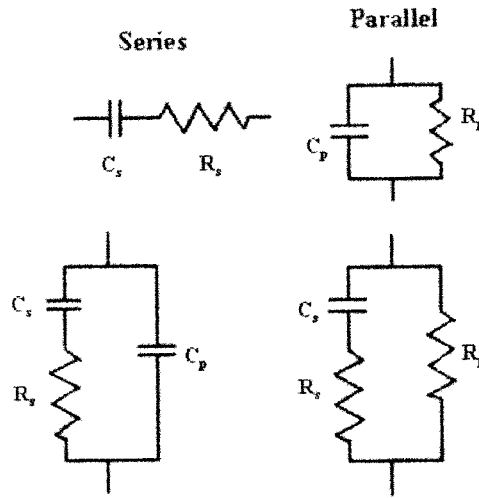
4.3.2 PARALLEL EQUIVALENT CIRCUIT

A capacitance C_p in parallel with a resistance R_p may also be used as a equivalent circuit (fig. 4.3). The admittance of the parallel circuit is given by

$$Y = j\omega C_p + \frac{1}{R_p} \quad (4.18)$$

The admittance of the capacitor with the dielectric is given by

$$Y = j\omega C_0(\epsilon' - j\epsilon'') \quad (4.19)$$



Variations of series-parallel equivalent

Fig. 4.3 Equivalent circuits of a lossy dielectric.

Equating the admittances and separating the real and imaginary parts gives

$$\varepsilon' = \frac{C_p}{C_o}; \quad \varepsilon'' = \frac{1}{\omega R C_o}; \quad \tan \delta = \frac{1}{\omega R C_p} \quad (4.20)$$

Equation (4.20) shows that the ε'' - ω curve shows a monotonic decrease. It is clear that a wide range of characteristics can be obtained by combining the series and parallel behavior. Table 4.1 gives the parameters for series and parallel equivalent.

Table 4.1
Equivalent circuit parameters

Series circuit	Parallel equivalent
R_s	$R_p = \frac{1 + \omega^2 C_s^2 R_s^2}{\omega^2 R_s C_s^2}$
$\tan \delta = \omega C_s R_s$	$\tan \delta = \frac{1}{\omega C_p R_p}$
Parallel circuit	Series equivalent
R_p	$R_s = \frac{R_p}{1 + \omega^2 C_p^2 R_p^2}$

4.3.3 SERIES-PARALLEL CIRCUIT

Fig. 4.3 also shows a series-parallel circuit in which a series branch having a capacitance C_s and a resistance R_s is in parallel with a capacitance C_p . We follow the same procedure to determine the real and imaginary parts of the complex dielectric constant ϵ^* . The admittance of the equivalent circuit is:

$$Y_{eq} = j\omega C_p + \frac{j\omega C_s}{(1 + j\omega C_s R_s)} \quad (4.21)$$

Substituting again $C_s R_s = \tau$ the above equation becomes

$$Y_{eq} = \frac{\omega^2 C_s R_s}{1 + \omega^2 \tau^2} + j\omega C_p + \frac{j\omega C_s}{1 + \omega^2 \tau^2} \quad (4.22)$$

Equating equations (4.22) and (4.19) we obtain

$$Y = j\omega \epsilon^* C_0 = j\omega C_0 (\epsilon' - j\epsilon'') \quad (4.23)$$

Separating the real and imaginary parts yields we obtain the equations:

$$\epsilon' = \frac{C_p}{C_0} + \frac{C_s}{C_0} \frac{1}{1 + \omega^2 \tau^2} \quad (4.24)$$

$$\epsilon'' = \frac{C_s}{C_0} \frac{\omega \tau}{1 + \omega^2 \tau^2} \quad (4.25)$$

From these two equations the power factor may be obtained as

$$\tan \delta = \frac{\epsilon''}{\epsilon'} = \frac{\omega \tau}{1 + \frac{C_p}{C_s} (1 + \omega^2 \tau^2)} \quad (4.26)$$

These equations may be simplified by substituting conditions that apply at the limiting values of ω .

(a) At $\omega = 0$, $\epsilon'' = 0$ and ϵ' has a maximum value given by

$$\varepsilon' = \frac{C_p}{C_0} + \frac{C_s}{C_0} = \varepsilon_s \quad (4.27)$$

(b) As $\omega \rightarrow \infty$, ε' approaches a minimum value given by

$$\varepsilon' = \frac{C_p}{C_0} = \varepsilon_\infty \quad (4.28)$$

(c) The radian frequency at which ε'' is a maximum is given by

$$\frac{\delta \varepsilon''}{\delta \omega} = C_0(1 + \omega^2 \tau^2)C_s - 2\omega^2 C_0 C_s \tau^2 = 0$$

which yields

$$\omega \tau = 1 \quad (4.29)$$

This result shows that the equivalent circuit yields $\omega_{\max}$ that is identical to the Debye criterion.

Substituting Equations (4.27) - (4.28) in equations (4.24) - (4.26) we get

$$\varepsilon' = \varepsilon_\infty + (\varepsilon_s - \varepsilon_\infty) \frac{1}{\omega^2 \tau^2} \quad (4.30)$$

$$\varepsilon'' = (\varepsilon_s - \varepsilon_\infty) \frac{\omega \tau}{1 + \omega^2 \tau^2} \quad (4.31)$$

$$\tan \delta = \frac{(\varepsilon_s - \varepsilon_\infty) \omega \tau}{\varepsilon_s + \varepsilon_\infty \omega^2 \tau^2} \quad (4.32)$$

These are identical with Debye equations providing a basis for the use of the equivalent circuit for polar dielectrics. The parameters of the equivalent circuit may be obtained by the relationships

$$\varepsilon''_{\max} = \frac{1}{2} \frac{C_s}{C_0} \quad (4.33)$$

$$\varepsilon_{\infty} = \frac{C_p}{C_0} \quad (4.34)$$

$$R_s = \frac{1}{\omega C_s} \quad (4.35)$$

We can also prove, by a similar approach, that the a series branch of C_s and R_s in parallel with R_p yields the Debye equations.

4.3.4 SUMMARY OF SIMPLE EQUIVALENT CIRCUITS

Fig. 4.4 shows a few simple circuits (I column), Z , the impedance (II column), Y , the admittance (III column), C^* , the complex capacitance (IV column) defined as

$$C^* = C'' - jC' = \varepsilon_0 \frac{A}{d} (\varepsilon' - j\varepsilon'') \quad (4.36)$$

χ' , χ'' in the frequency domain (V column). The real and imaginary parts are plotted for Z , Y , C^* as in the complex plane plots¹³. A brief description of each row is given below.

(a) A series circuit with two energy storage elements L and C . The energy is exchanged between the inductive and capacitive elements in a series of periodic oscillations that get damped due to the resistance in the circuit. Resonance occurs in the circuit when the inductive reactance X_L equals the capacitive reactance X_C and the circuit behaves, at the resonance frequency, as though it is entirely resistive. The current in the circuit is then limited only by the resistance. In dielectric studies resonance phenomenon is referred to as absorption and is discussed in greater detail in section 4.6.

(b) A series RC circuit. $X_C = 1/j\omega C$ decreases with increasing frequency. The Cole-Cole plots of Y and C^* are semi-circles and Debye relaxation applies. This circuit has been discussed in section 4.3.1.

(c) A parallel combination of R and C , representing a leaky capacitor. The Cole-Cole plot of Z is a semi-circle while ε'' - ω plot decreases monotonically. This circuit has been analysed in section 4.3.2.

(d) A series RC circuit in parallel with a capacitance, C_{∞} . A series RC circuit has been shown to exhibit Debye relaxation. The capacitance in parallel represents any frequency independent process that operates jointly with the Debye process. The Cole-Cole plot of Y shows a upturn due to the additional admittance of the parallel capacitor. The limiting values of capacitance, that is the intercept on the real axis are $C+C_{\infty}$ and C_{∞} . The ε'' - ω peak is shifted higher and the ε' - ω curve has a limiting value due to ε_{∞} .

- (e) A parallel RC circuit in series with a resistance. An inflection in the loss factor at frequencies lower than ω_p is the dominant characteristic of this circuit.
- (f) A parallel RC circuit in series with a capacitance. The response is similar to that shown in (d) with the Cole-Cole plot showing a upturn due to the series capacitance which ‘resembles’ a series barrier.
- (g) Two parallel RC circuits in series. This is known as interfacial polarization and is considered in detail in the next section. The increase in ϵ'' at lower frequencies is similar to (e) above.
- (h) The last entry is in a different category than the lumped elements adopted in the equivalent circuits so far. The so-called transmission line equations are derived using the concept that the circuit parameters, R, L and C, are distributed in practice. In the case of dielectric materials we can use only R and C as distributed, as in the case of a capacitor with electrodes providing a high sheet resistance¹⁴. In one dimension let r and c be resistance and capacitance per unit length respectively.

The differential equations for voltage and current at a distance x are

$$dV = I(x)r dx \quad (4.37)$$

$$dI = j\omega c V(x) dx \quad (4.38)$$

Equations (4.37) and (4.38) result in differential equations for V:

$$\frac{d^2 V}{dx^2} = A^2 V(x) \quad (4.39)$$

where

$$A = (1 + j) \left(\frac{\omega r c}{2} \right)^{1/2} \quad (4.40)$$

The solution of equation (4.39) is

$$V(x) = V_0 (\cosh Ax - B \sinh Ax) \quad (4.41)$$

where V_0 is the input voltage and B is a constant determined by the boundary conditions. For an infinitely long line $B = 1$. The current is given by equation (4.37) as

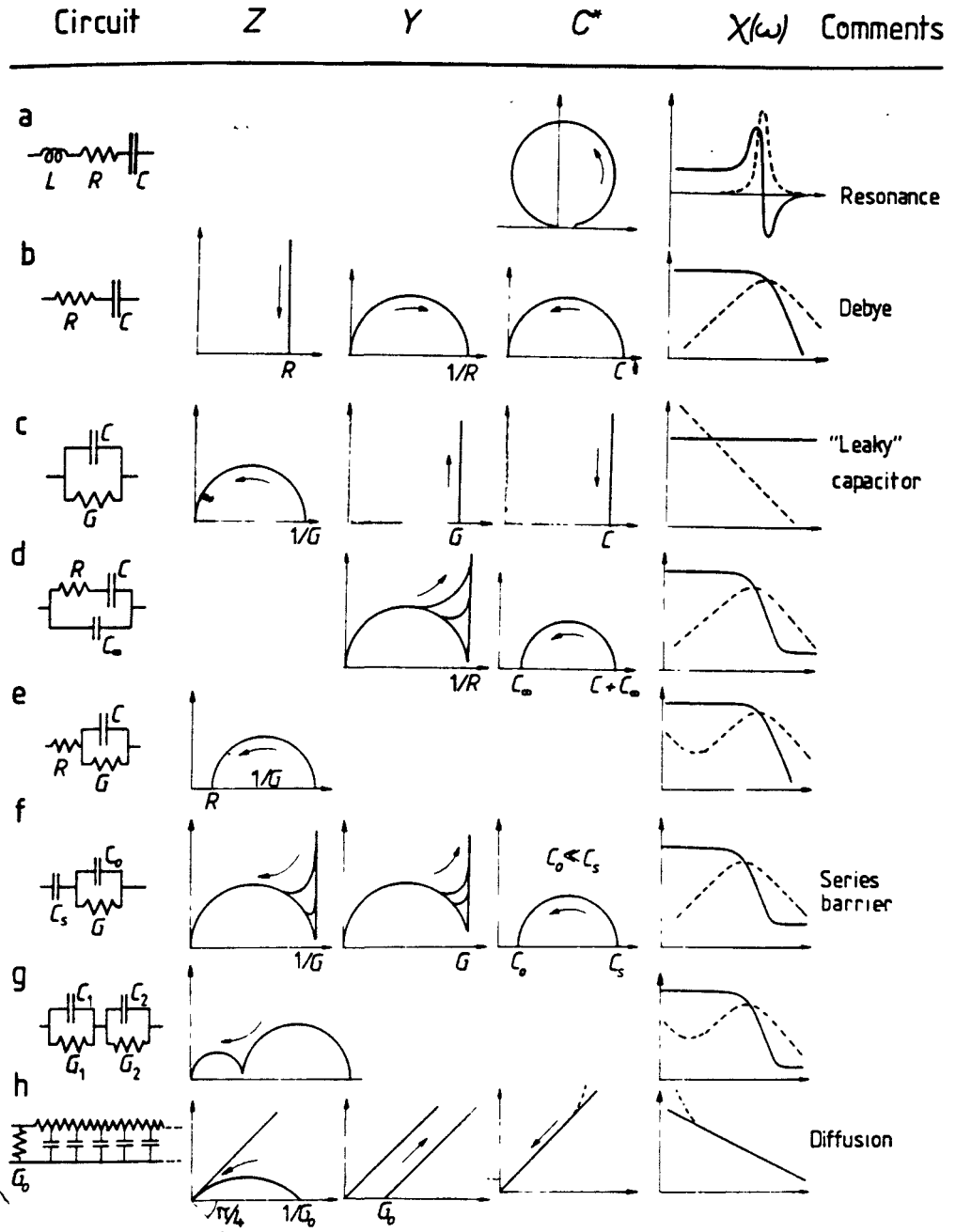


Fig. 4.4 Schematic representations of the equivalent simple circuits, see text (Jonscher, 1983; Chelsea Dielectric).

$$I(x) = \frac{1}{r} \frac{dV}{dx} = \frac{V_0 A}{r} (\sinh Ax - \cosh Ax) \quad (4.42)$$

The input current I_0 is obtained by substituting $x = 0$, as

$$I_0 = \frac{V_0 A}{r} \quad (4.43)$$

The input admittance of an infinitely long line is the ratio I_0/V_0 , giving

$$Y = \frac{A}{r} = \left(\frac{c}{2r} \right)^{1/2} \omega^{1/2} (1 + j) \quad (4.44)$$

The Cole-Cole plot of the admittance is a straight line with a slope of one or making an angle of $\pi/4$ with the real axis (see column 3, row h in fig. 4.4). If there is a parallel dc conductance the line through the origin will be displaced to the right. The real and complex part of the dielectric constant in the frequency domain are shown by the same line with slope of $-1/2$ as shown in the last column of row h . The dashed upward tilt at low frequencies is due to the additional parallel conductance, if present. Lack of peak in this situation is particularly interesting.

4.4 INTERFACIAL POLARIZATION

Interfacial polarization, also known as space charge polarization, arises as a result of accumulation of charges locally as they drift through the material. In this respect, this kind of polarization is different from the three previously discussed mechanisms, namely, the electronic, orientational and atomic polarization, all of which are due to displacement of bound charges. The atoms or molecules are subject to a locally distorted electric field that is the sum of the applied field and various distortion mechanisms apply. In the case of interfacial polarization large scale distortions of the field takes place. For example, charges pile up in the volume or on the surface of the dielectric, predominantly due to change in conductivity that occurs at boundaries, imperfections such as cracks and defects, and boundary regions between the crystalline and amorphous regions within the same polymer. Regions of occluded moisture also cause an increase in conductivity locally, leading to accumulation of charges.

We consider the classic example of Maxwell-Wagner to derive the $\epsilon' - \omega$ and $\epsilon'' - \omega$ characteristics due to the interfacial polarization that exists between two layers of dielectric materials that have different conductivity. Let d_1 and d_2 be the thickness of two materials that are in series. Their dielectric constant and resistivity are respectively ϵ and ρ , with subscripts 1 and 2 denoting each material (Fig. 4.5).

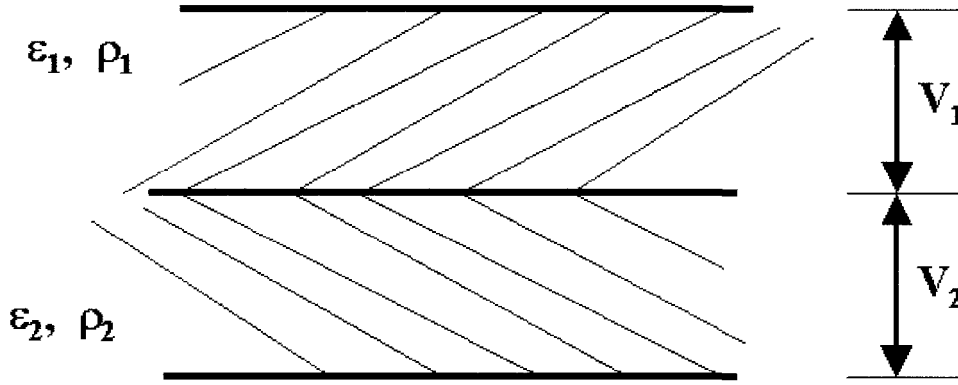


Fig. 4.5 Dielectrics with different conductivities in series.

When a direct voltage, V , is applied across the combination the voltage across each dielectric will be distributed, at $t = 0_+$, according to

$$V_{10} = V \frac{C_2}{C_1 + C_2} \quad (4.45)$$

$$V_{20} = V \frac{C_1}{C_1 + C_2} \quad (4.46)$$

When a steady state is reached at $t = \infty$ the voltage across each dielectric will be

$$V_{1\infty} = V \frac{R_1}{R_1 + R_2} \quad ; \quad V_{2\infty} = V \frac{R_2}{R_1 + R_2} \quad (4.47)$$

The charge stored in each dielectric will change during the transition period. At $t = 0_+$ the charge in each layer will be equal;

$$Q_{10} = Q_{20} = C_1 V_{10} = C_2 V_{20} = \frac{C_1 C_2}{C_1 + C_2} V \quad (4.48)$$

At $t = \infty$ the charge in each layer will be

$$Q_{1\infty} = C_1 V_{1\infty} = \frac{C_1 R_1}{R_1 + R_2} V; \quad Q_{2\infty} = C_2 V_{2\infty} = \frac{C_2 R_2}{R_1 + R_2} V \quad (4.49)$$

During the transition period the change in the stored charge in each layer is:

$$\Delta Q_1 = Q_{1\infty} - Q_{10} = VC_1 \frac{(R_1 C_1 - R_2 C_2)}{(R_1 + R_2)(C_1 + C_2)} \quad (4.50)$$

$$\Delta Q_2 = Q_{2\infty} - Q_{20} = VC_2 \frac{(R_2 C_2 - R_1 C_1)}{(R_1 + R_2)(C_1 + C_2)} \quad (4.51)$$

The redistribution of charges within the layers occurs due to migration of charges and equations (4.50) and (4.51) show that there will be no migration of charges if the condition $C_1 R_1 = C_2 R_2$ is satisfied. Since $C_1 R_1 = \varepsilon_0 \varepsilon_1 \rho_1$ and $C_2 R_2 = \varepsilon_0 \varepsilon_2 \rho_2$ the condition for migration of charges translates into

$$\varepsilon_1 \rho_1 \neq \varepsilon_2 \rho_2 \quad (4.52)$$

Let us suppose that the condition set by expression (4.52) is satisfied by the components of the two layer dielectric. The frequency response of the series combination may be calculated by the method outlined in the previous section. The admittance of the equivalent circuit (fig. 4. 6) is given by

$$Y_{eq} = \frac{Y_1 Y_2}{Y_1 + Y_2} \quad (4.53)$$

where

$$Y_1 = \frac{1}{R_1} + j\omega C_1 \quad (4.54)$$

$$Y_2 = \frac{1}{R_2} + j\omega C_2 \quad (4.55)$$

leading to

$$Y_{eq} = \frac{(1 + j\omega\tau_1)(1 + j\omega\tau_2)}{R_1 + R_2 + j\omega R_1 R_2 (C_1 + C_2)} \quad (4.56)$$

where we have made the substitutions

$$C_1 R_1 = \tau_1; \quad C_2 R_2 = \tau_2 \quad (4.57)$$

We further substitute

$$\tau = \frac{(C_1 + C_2)R_1R_2}{R_1 + R_2} = \frac{R_1\tau_1 + R_2\tau_2}{R_1 + R_2} \quad (4.58)$$

Substituting equations (4.57) and (4.58) into (4.56) and rationalizing the resultant expression yields a rather a long expression:

$$Y_{eq} = \frac{1}{R_1 + R_2} \times \frac{[1 - \omega^2\tau_1\tau_2 + \omega^2\tau(\tau_1 + \tau_2) - j\omega\tau(1 - \omega^2\tau_1\tau_2) + j\omega(\tau_1 + \tau_2)]}{1 + \omega^2\tau^2} \quad (4.59)$$

The admittance of the capacitor with the real dielectric is

$$Y = j\omega C_0 \epsilon^* = j\omega C_0 (\epsilon' - j\epsilon'') \quad (4.60)$$

where ϵ^* is the complex dielectric constant of the series combination of dielectrics.

Equating the real and imaginary parts of (4.59) and (4.60) we get

$$\epsilon' = \frac{1}{C_0(R_1 + R_2)} \frac{[(\tau_1 + \tau_2) - \tau(1 - \omega^2\tau_1\tau_2)]}{1 + \omega^2\tau^2} \quad (4.61)$$

$$\epsilon'' = \frac{1}{\omega C_0(R_1 + R_2)} \frac{[1 - \omega^2\tau_1\tau_2 + \omega^2\tau(\tau_1 + \tau_2)]}{1 + \omega^2\tau^2} \quad (4.62)$$

(a) When $\omega = 0$ equation (4.61) reduces to

$$\epsilon' = \epsilon_s = \frac{\tau_1 + \tau_2 - \tau}{C_0(R_1 + R_2)} \quad (4.63)$$

(b) As $\omega \rightarrow \infty$

$$\epsilon' = \epsilon_\infty = \frac{\tau_1\tau_2}{\tau} \frac{1}{C_0(R_1 + R_2)} \quad (4.64)$$

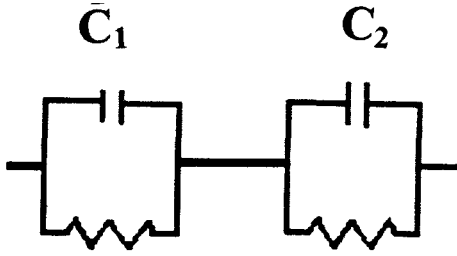


Fig. 4.6 Equivalent circuit for two dielectrics in series for interfacial polarization.

Substituting equations (4.63) and (4.64) in (4.61) we get

$$\epsilon' = \epsilon_{\infty} + \frac{\epsilon_s - \epsilon_{\infty}}{1 + \omega^2 \tau^2} \quad (4.65)$$

A further substitution of equations (4.63) and (4.64) into equation (4.62) gives

$$\epsilon'' = \frac{1}{\omega C_0 (R_1 + R_2)} + \frac{\omega \tau (\epsilon_s - \epsilon_{\infty})}{1 + \omega^2 \tau^2} \quad (4.66)$$

Equation (4.65) gives the $\epsilon' - \omega$ characteristics for interfacial polarization. It is identical to the Debye equation (3.28), that is, the dispersion for interfacial polarization is identical with dipolar dispersion although the relaxation time for the former could be much longer. It can be as large as a few seconds in some heterogeneous materials. The relaxation spectrum given by equation (4.66) has two terms; the second term is identical to the Debye relaxation (equation 3.29) and at higher frequencies the relaxation for interfacial polarization is indistinguishable from dipolar relaxation. However the first term, due to conductivity, makes an increasing contribution to the dielectric loss as the frequency becomes smaller, Fig. 4.7¹⁵

The complex dielectric constant of the two layer dielectric including the effects of conductivity is given by

$$\epsilon^* = \epsilon_{\infty} + \frac{\epsilon_s - \epsilon_{\infty}}{1 + j\omega\tau} - j \frac{\sigma_{dc}}{\omega \epsilon_0} \quad (4.67)$$

The conductivity term (σ / ω) and not the conductivity itself, increases with decreasing ω . An increase in absorbed moisture or in the case of polymers, the onset of d.c. conductivity at higher temperatures, dramatically increases the loss factor at lower

frequencies. As stated above, the relaxation time for interfacial polarization can be as large as a few seconds in heterogeneous and semi-crystalline polymers. Such behavior is observed in polyethylene terephthalate (PET), which is semi-crystalline.

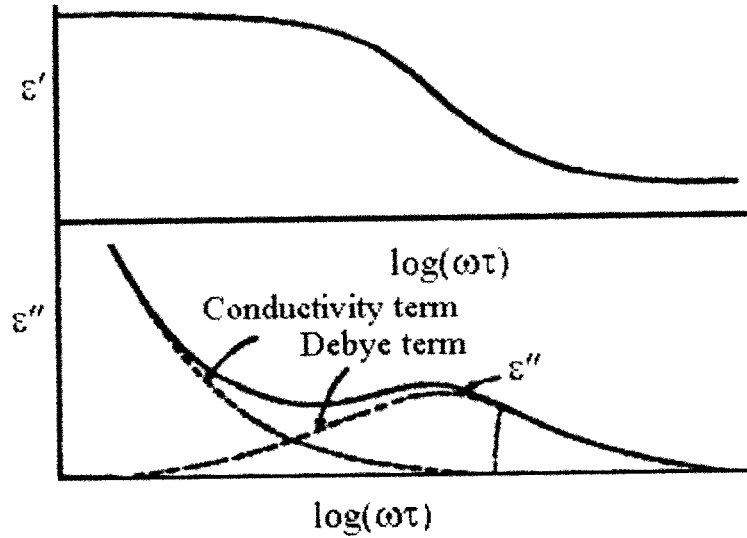


Fig. 4.7 Relaxation spectrum of a two layer dielectric. The conductivity is given by $\sigma = \epsilon_0 / C_0(R_1 + R_2)$.

Fig. 4.8 shows the measured ϵ' and ϵ'' as a function of frequency at various temperatures in the range 150-190°C¹⁶. As the frequency is reduced below ~100 Hz both ϵ' and ϵ'' increase significantly, with ϵ' reaching values as high as 1000 at 10⁻² Hz. This effect is attributed to the interfacial polarization that occurs in the boundaries separating the crystalline and non-crystalline regions, the former region having much higher resistivity. As the frequency increases the time available for the drift of charge carriers is reduced and the observed increase in ϵ' and ϵ'' is substantially less. Space charge polarization at electrodes is also considered to be a contributing factor at low frequencies for the increase in ϵ' .

The two layer model with each layer having a dielectric constant of ϵ_1 and ϵ_2 and direct current conductivity of σ_1 and σ_2 , in series, has been analyzed by Volger¹⁷. The frequency dependent behavior of this model is obtained in terms of the following equations:

$$\epsilon'(\omega) = \epsilon_\infty + \frac{(\epsilon_s - \epsilon_\infty)}{1 + \omega^2 \tau^2} \quad (4.68)$$

In equation (4.68) the following relationships hold:

$$\varepsilon_s = \frac{(d_1 + d_2)}{(d_1 \rho_1 + d_2 \rho_2)^2} (d_1 \varepsilon_1 \rho_1^2 + d_2 \varepsilon_2 \rho_2^2) \quad (4.69)$$

$$\varepsilon_\infty = \frac{\frac{d_1 + d_2}{d_1} + \frac{d_2}{d_2}}{\frac{\varepsilon_1}{\varepsilon_1} + \frac{\varepsilon_2}{\varepsilon_2}} \quad (4.70)$$

The inset of fig. 4.9 defines the quantities in equation (4.69).

The conductivity and resistivities are also complex quantities and their relationships to the same quantities of the individual dielectrics are given by:

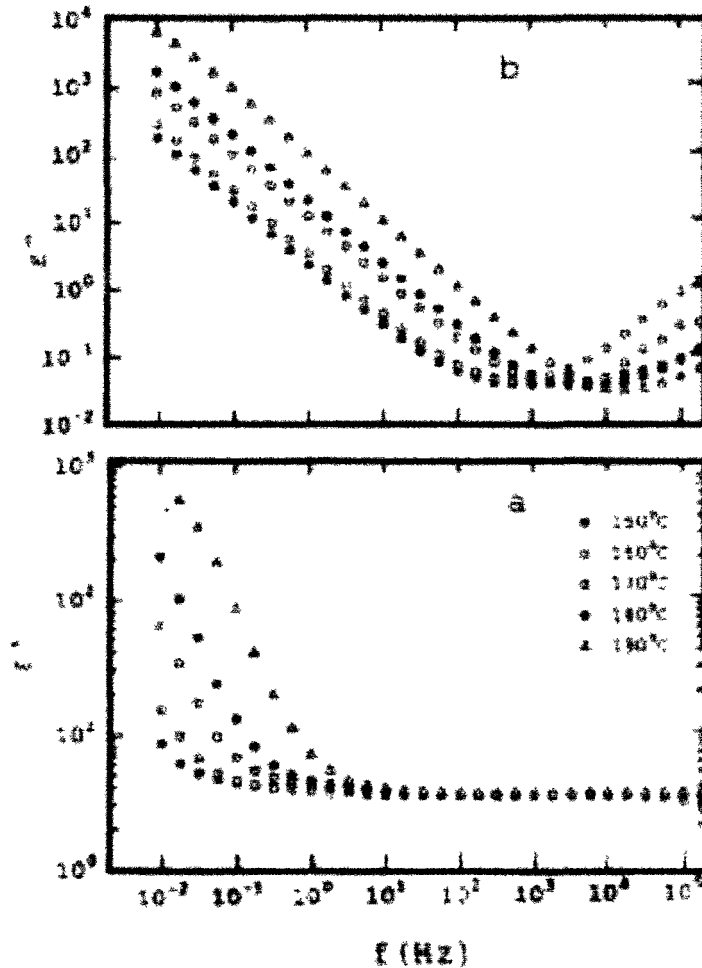


Fig. 4.8 The (a) real and (b) imaginary part of the complex dielectric constant in PET at various temperatures (Neagu et. al., 1997, with permission of the Institute of Phys., UK)

$$\sigma'(\omega) = \frac{\sigma_s + \sigma_\infty \tau_\sigma^2 \omega^2}{1 + \tau_\sigma^2 \omega^2} \quad (4.71)$$

where

$$\sigma_s = \frac{d_1 + d_2}{d_1 \rho_1 + d_2 \rho_2} \quad (4.72)$$

$$\sigma_\infty = \frac{d_1 + d_2}{\left(\frac{d_1}{\epsilon_1} + \frac{d_2}{\epsilon_2}\right)^2} \left(\frac{d_1 \sigma_1}{\epsilon_1^2} + \frac{d_2 \sigma_2}{\epsilon_2^2} \right) \quad (4.73)$$

Further we have the following two relationships

$$\rho'(\omega) = \rho_\infty + \frac{(\rho_s - \rho_\infty)}{1 + \omega^2 \tau_\rho^2} \quad (4.74)$$

$$\tan \delta = \frac{\sigma_\infty}{\epsilon_o \omega \epsilon_\infty} \frac{\left(\frac{\epsilon_\infty \sigma_s}{\epsilon_s \sigma_\infty} \right) + \omega^2 \tau_\delta^2}{1 + \omega^2 \tau_\delta^2} \quad (4.75)$$

Fig. 4.-9 shows these relationships and the similarity between $\epsilon'(\omega)$ and $\rho'(\omega)$ is evident. The relaxation time for each process is different and the relationship between them is given by the equation

$$\tau = \tau_\sigma = \tau_\rho \left(\frac{\sigma_s}{\sigma_\infty} \right)^{1/2} = \tau_\delta \left(\frac{\epsilon_s}{\epsilon_\infty} \right)^{1/2}$$

The increase in dielectric constant, ϵ' , at low frequencies as shown in fig. 4.8 cannot be attributed to conductivity and the observed effect is possibly due to the accumulation of charges at the electrodes. The real part of conductivity, σ' , remains constant at low frequencies, increasing to a saturation value at high frequencies. The low frequency flat part is almost equal to dc conductivity and may not be observed except at high temperatures. Fig. 4.10 demonstrates such conductivity behavior.

4.5 THE ABSORPTION PHENOMENON

So far, our discussion has been restricted to dielectric relaxation that occurs at frequencies generally below 100 GHz. This frequency limit encompasses most of the dipolar and interfacial mechanisms. The frequency dependence of atomic polarizability becomes evident at infrared frequencies ($\sim 10^{12}$ Hz); the frequency dependence of electronic polarizability becomes evident at optical frequencies. Considering the latter, the electron cloud, due to its negligible mass relative to the atom or molecule, is, capable of keeping in phase with the alternating nature of the voltage well into the range of 10^{15} Hz (100 nm).

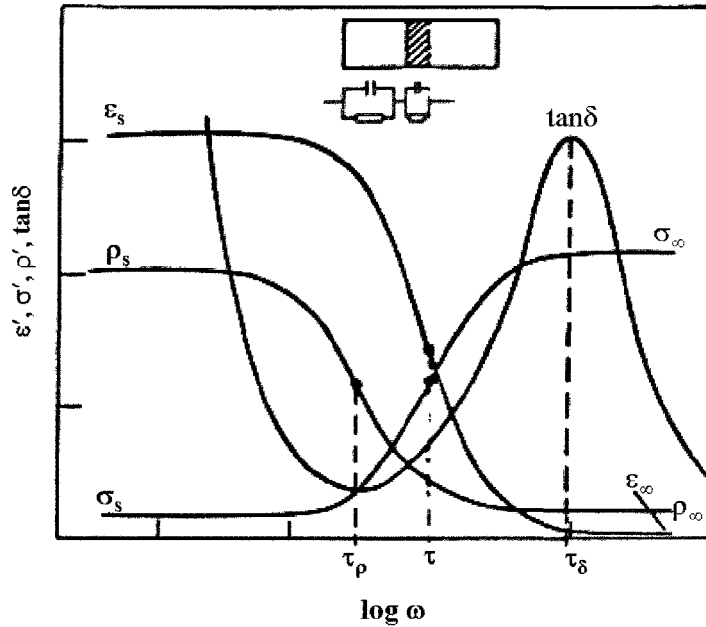


Fig. 4.9 Calculated curves giving the dependence of ϵ' , σ' , ρ' and $\tan\delta$ on $\log \omega$ in the two layer model of Volger [17]. Arbitrary units. (with permission of Academic Press).

The oscillating electron bound elastically to an equilibrium position can be viewed as a harmonic oscillator and when the exciting frequency coincides with the natural frequency of the oscillator, resonance occurs. In dielectric studies ϵ' - ω characteristic at resonance is known as **anomalous dispersion** and ϵ'' - ω characteristic is known as absorption phenomenon. The equation of motion of a linear harmonic oscillator is

$$m \frac{d^2 x}{dt^2} + ax = 0 \quad (4.76)$$

where m is the electron mass, x and t are the position and time variables, and a is a constant not to be confused with acceleration.

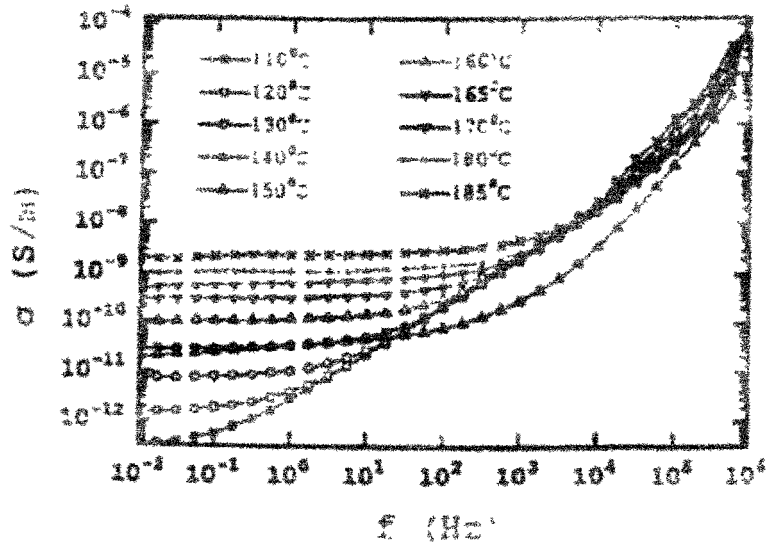


Fig. 4.10 The real part of AC conductivity (σ') versus frequency at various temperatures. The flat region at low frequencies, particularly at high temperatures gives approximate dc conductivity. Compare with theoretical curve shown in fig. 4-9 (Neagu et. al., 1997) (with permission of IEEE)

The solution of equation (4.76) is

$$x = x_0 \cos \omega_0 t \quad (4.77)$$

where

$$\omega_0 = (a/m)^{1/2} \quad (4.78)$$

is the characteristic frequency of the harmonic oscillator. If the applied field is represented by

$$E = E_{\max} \cos \omega t \quad (4.79)$$

where ω is the radian frequency; the force on the electron due to the applied field is

$$F = eE_{\max} \cos \omega t \quad (4.80)$$

where e is the electronic charge. The equation for the harmonic oscillator with the force acting on the electron is

$$m \frac{d^2 x}{dt^2} + ax = eE_{\max} \cos \omega t \quad (4.81)$$

The solution of this equation is

$$x = A \cos \omega t \quad (4.82)$$

where A is a constant, obtained from

$$-\omega^2 mA + a A = eE_{\max} \quad (4.83)$$

Expressing m in terms of the characteristic frequency and rearranging equation (4.83) we get

$$A(\omega^2 - \omega_0^2) = \frac{e}{m} E_{\max} \quad (4.84)$$

The solution of equation (4.81) is obtained as

$$x = \frac{eE_{\max}}{m(\omega_0^2 - \omega^2)} \cos \omega t \quad (4.85)$$

Recalling that the induced dipole moment due to electronic polarizability is the product of the electronic charge and the displacement, we get the induced dipole moment as

$$\mu_{ind} = e x = \frac{e^2 E_{\max}}{m(\omega_0^2 - \omega^2)} \cos \omega t = \frac{e^2}{m(\omega_0^2 - \omega^2)} E \quad (4.86)$$

The induced electronic polarizability is obtained as

$$\alpha_e = \frac{\mu_{ind}}{E} = \frac{e^2}{m(\omega_0^2 - \omega^2)} \quad (4.87)$$

By substituting typical values, $e = 1.6 \times 10^{-19}$ C, $m = 9.1 \times 10^{-31}$ kg, $\alpha_e = 5 \times 10^{-40}$ F/m², $\omega = 10^9$ s⁻¹ we get $\omega_0 \sim 10^{16}$ s⁻¹, which falls in the ultra-violet part of the spectrum.

Using equation (4.87) the variation of α_e with ω may be shown to have the following characteristics: when $\omega_0 \gg \omega$, α_e has relatively small value. As ω_0 approaches ω , α_e and therefore ϵ' , increase sharply, reaching theoretically an infinite value at $\omega_0 = \omega$. For a further increase in ω , that is $\omega_0 < \omega$, α_e becomes negative. When $\omega = \omega_0 + \Delta\omega$ an increase

in ω results in a decrease of α_e . So this behavior is usually referred to as anomalous dispersion. In practice the α_e - ω characteristics will be modified considerably due to the fact that the motion of electron is subject to a damping effect which was not taken into account in formulating equation (4.76).

The oscillating electron will generate electromagnetic radiation that acts as a damping force. From mechanics we know that the damping factor in a linear harmonic oscillator is proportional to the electron velocity. The equation of motion of the electron is modified as

$$m \frac{d^2 x}{dt^2} + b \frac{dx}{dt} + ax = eE_{\max} \cos \omega t \quad (4.88)$$

We shall assume that the solution is of the form

$$x = A \cos \omega t = Ae^{j\omega t} \quad (4.89)$$

remembering to consider only the real part of the solution.

Substitution of equation (4.89) in (4.88) gives

$$(-\omega^2 A + \frac{aA}{m} + j \frac{\omega bA}{m} - \frac{e}{m} E_{\max}) e^{j\omega t} = 0 \quad (4.90)$$

Equation (4.90) is identical to equation (4.83) except for the term containing b . Following a procedure similar to the one adopted for the no-damping situation we get

$$A = \frac{e}{m} \frac{E_{\max}}{(\omega_0^2 - \omega^2 + j\omega_0 / m)} \quad (4.91)$$

where $\omega_0 = \sqrt{\frac{a}{m}}$.

Hence

$$x = \frac{e}{m} \frac{E_{\max}}{(\omega_0^2 - \omega^2 + j\omega b / m)} e^{j\omega t} \quad (4.92)$$

Equation (4.92) shows that the displacement is out of phase with the applied field and therefore we must introduce a complex polarizability defined by

$$\alpha_e^* = \alpha_e' - j\alpha_e'' \quad (4.93)$$

The induced dipole moment is

$$\mu_e = e x = \frac{e^2}{m} \frac{E_{\max}}{(\omega_0^2 - \omega^2 + j\omega b/m)} e^{j\omega t} \quad (4.94)$$

The induced polarizability is

$$\alpha_e^* = \frac{e^2}{m} \frac{1}{(\omega_0^2 - \omega^2 + j\omega b/m)} \quad (4.95)$$

Separating the real and imaginary parts we obtain the pair of equations

$$\alpha_e' = \frac{e^2}{m} \frac{(\omega_0^2 - \omega^2)}{(\omega_0^2 - \omega^2)^2 + (\omega b/m)^2} \quad (4.96)$$

$$\alpha_e'' = \frac{e^2}{m} \frac{(\omega b/m)}{(\omega_0^2 - \omega^2)^2 + (\omega b/m)^2} \quad (4.97)$$

From these equations we deduce the following:

(a) At $\omega = 0$ the real part

$$\alpha_e' = \frac{e^2}{m} \frac{1}{\omega_0^2} \quad (4.98)$$

which is identical to equation (4.87) with $b = 0$. The polarizability is in phase with the applied field. Of course, $\alpha_e'' = 0$.

(b) $\omega \ll \omega_0$, both α_e' and α_e'' are positive.

(c) At $\omega = \omega_0$, α_e' sharply falls to zero and α_e'' has a peak value of $e^2/\omega b$.

(d) For $\omega > \omega_0$, α_e' is negative and α_e'' is positive.

(e) α_e' has a maximum value when $\omega_0 - \omega = \Delta\omega$ is $b/2m$. It has a minimum (negative) value when $\omega - \omega_0 = \Delta\omega$ is $b/2m$. Therefore the distance between the two peaks is b/m .

These characteristics are shown in Fig. 4. 11. It should be emphasized that $\alpha_e' - \omega$ and $\alpha_e'' - \omega$ characteristics depend on the damping factor. Fig. 4.12¹⁸ shows these characteristics for three values of the parameter ($k=b\omega_0/m$). For low damping factor, $k=0.1$, the characteristics are identical to that shown in Fig. 4.11. With greater damping, $k=1$, the negative undershoot of α_e' is reduced. With still greater value, $k=10$, the negative undershoot is completely suppressed. The characteristics also become broader as the damping increases.

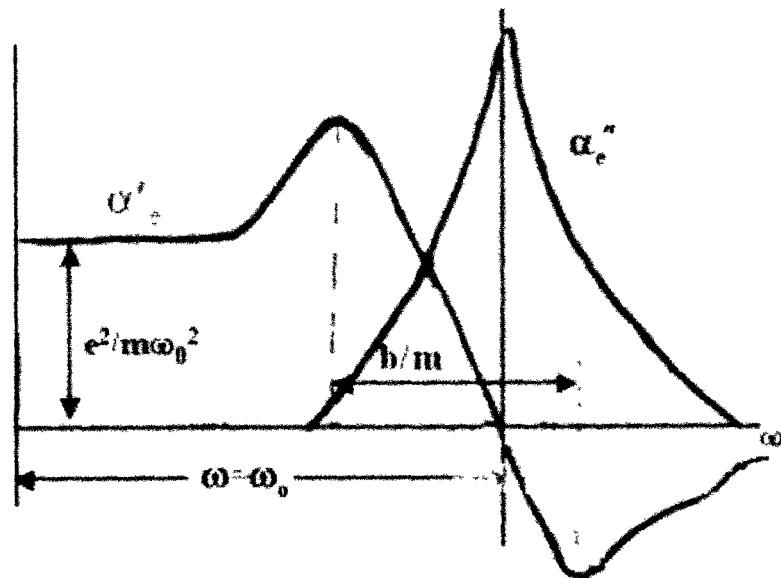


Fig. 4.11 Variation of the real and imaginary parts of the electronic polarizability with frequency.

The theory outlined above has been applied for the study of microwave absorption in gases leading to techniques such as microwave spectroscopy. In crystalline solids the absorption spectra are in the short wavelength regions for electronic transitions within individual atoms or molecules, and in the longer wave length due to vibrations of the crystal as a whole. The lattice vibrations fall into two categories, the optical and acoustical frequency. Acoustical vibrations do not cause a change in polarization and there will be no electromagnetic interaction. The optical vibrations are associated with the oscillatory motion of the charges.

In an ionic crystal the simplest oscillatory motion is due to the vibration of neighboring ions of opposite charges, such as the movement of K^+ and Cl^- ions, resembling a dipole of varying moment. The frequency of this oscillation is of the order of 10^{13} s. There are two basic types of vibrations. One, along the line joining the equilibrium positions of the charges, called **longitudinal optic mode (LO)** and another, in a plane perpendicular to the line joining the equilibrium positions. This mode which is much stronger is called **transverse optic mode (TO)**. Evidence for strong resonance absorption in TO mode in KCl at 7K has been reported by Parker et. al.¹⁹.

Extensive studies of infrared spectra have given data of inter-atomic forces and the shape of the electron distribution. A discussion of these are beyond the scope of this book.

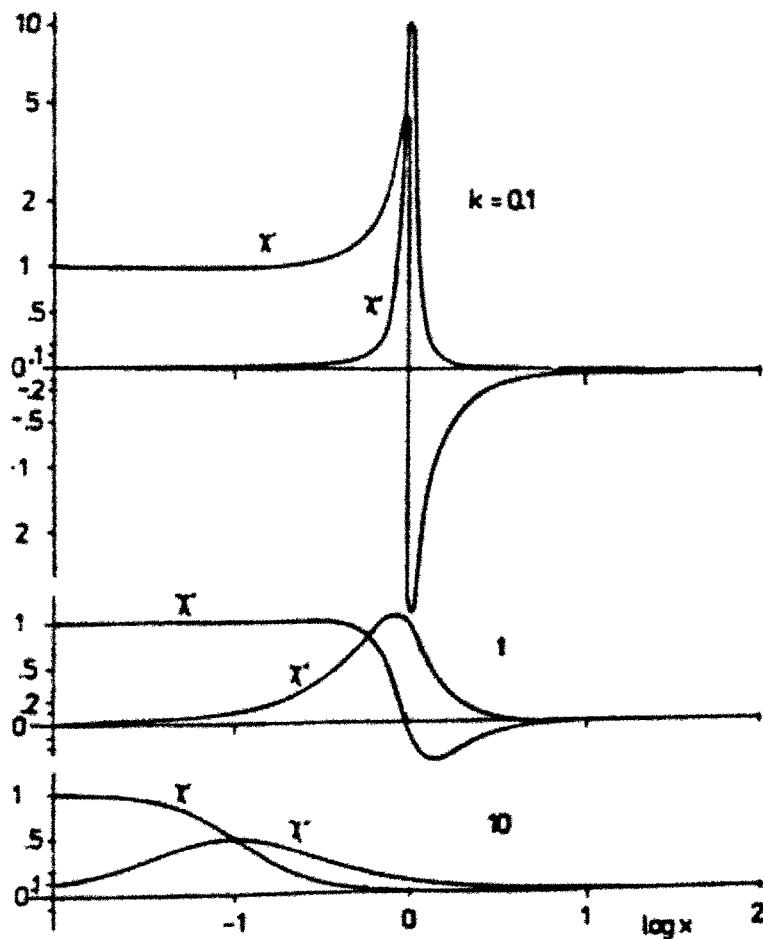


Fig. 4.12 Dispersion (real part) and absorption (imaginary part) of the susceptibility for three values of the damping coefficient as a function of $x = \omega/\omega_0$.

4.6 FREQUENCY DEPENDENCE OF ϵ^*

We are now in a position to represent the variation in the complex dielectric constant as a function of frequency, from $\omega = 0$ to $\omega \rightarrow \infty$. Fig. 4-13 shows the contribution of individual polarization mechanisms to the dielectric constant and their relaxation frequencies. As each process relaxes the dielectric constant becomes smaller because the contribution to polarization from that mechanism ceases. Beyond optical frequencies the dielectric constant is given by $\epsilon_\infty = n^2$.

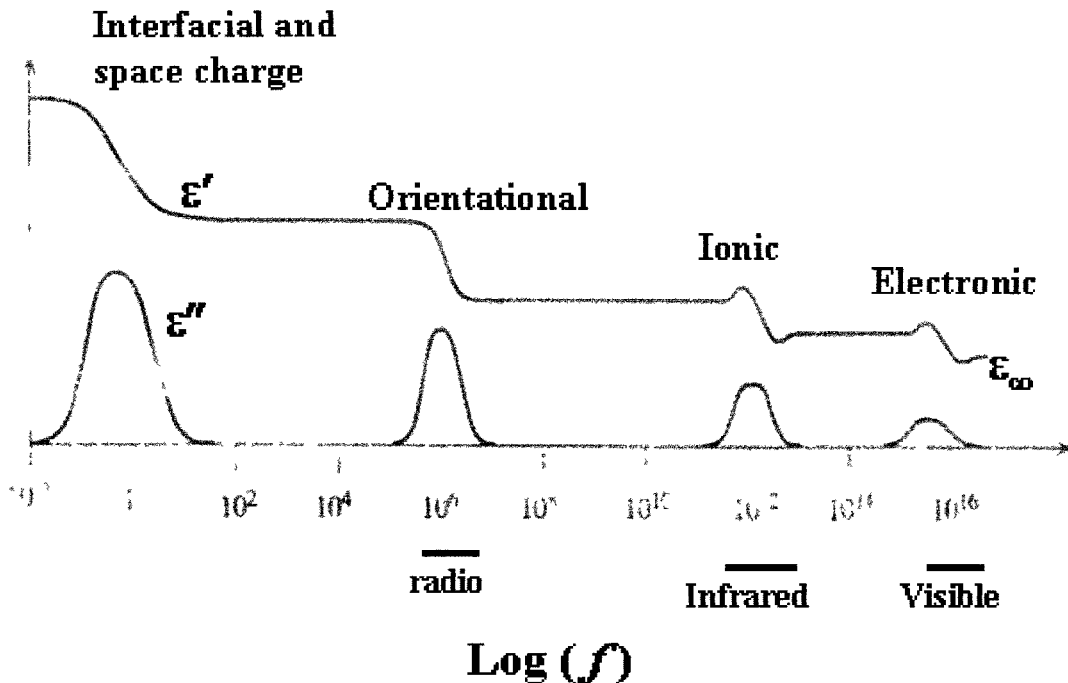


Fig. 4.13 Frequency dependence of the real and imaginary parts of the dielectric constant (schematic).

Though these mechanisms are shown, for the sake of clarity, as distinct and clearly separable, in reality the peaks are broader and often overlap. The space charge polarization may involve several mechanisms of charge build up at the electrode dielectric interface or in the amorphous and crystalline regions of a semi-crystalline polymer. Several types of charges may also be involved depending upon the mechanism of charge generation.

The orientational polarization occurs in the radio frequency to microwave frequency range in dipolar liquids. However in polymers the dipoles may be constrained to rotate or move to a limited extent depending upon whether the dipole is a part of the main chain or side group. Correspondingly the relaxation frequency may be smaller, of the order of a few hundred kHz. Further, in solids there is no single vibration frequency but only a range of allowed frequencies, making the present treatment considerably simplified. The experimental results presented in the next chapter in a number of different polymers will make this evident.

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